

Mixed Sandwich Imido Complexes of Uranium(V) and Uranium(IV): Synthesis, Structure and Redox Behaviour[#]

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Abstract

The mixed sandwich U(III) complex $\{U[\eta^8\text{-C}_8\text{H}_6(1,4\text{-Si}(^i\text{Pr})_3)_2](\text{Cp}^*)(\text{THF})\}$ reacts with the organic azides RN_3 ($\text{R} = \text{SiMe}_3$, 1-Ad, BMes_2) to afford the corresponding, structurally characterised U(V) imido complexes $\{U[\eta^8\text{-C}_8\text{H}_6(1,4\text{-Si}(^i\text{Pr})_3)_2](\text{Cp}^*)(\text{NR})\}$. In the case of $\text{R}=\text{SiMe}_3$, the reducing power of the U(III) complex leads to reductive coupling as a parallel minor reaction pathway, forming R-R and the U(IV) azide-bridged complex $\{[U]\}_2(\mu\text{-N}_3)_2$, along with the expected $[U]=\text{NR}$ complex. All three $[U]=\text{NR}$ complexes show a quasi-reversible one electron reduction between -1.6 to -1.75 V, and for $\text{R}=\text{SiMe}_3$, chemical reduction using K/Hg affords the anionic U(IV) complex $\text{K}^+\{U[\eta^8\text{-C}_8\text{H}_6(1,4\text{-Si}(^i\text{Pr})_3)_2](\text{Cp}^*)=\text{NSiMe}_3\}^-$. The molecular structure of the latter shows an extended structure in the solid state in which the K counter cations are successively sandwiched between the Cp^* ligand of one $[U]$ anion and the $\text{COT}^{\text{tips}2}$ ligand of the next.

Introduction

Low valent actinide (essentially uranium and thorium) chemistry has attracted significant attention, both from a purely academic viewpoint but also in the context of activation of important small molecules.¹ Examples of the latter include CO cyclo-oligomerisation,² CO_2 ³ and SO_2 ⁴ reductive coupling, NO/CO co-disproportionation,⁵ CO/ H_2 coupling,⁶ N_2 activation,⁷ and electro-catalytic splitting of H_2O promoted by sterically encumbered U(III) complexes.⁸ The common denominator amongst all these examples is that they employ the An(III)/An(IV) (An =

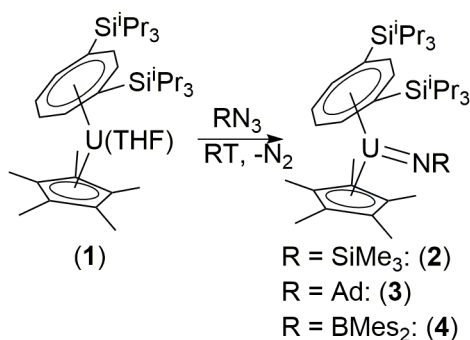
[#] Dedicated to Bill on the occasion of his 70th birthday - and wishing him many more!

U, Th) redox couple to promote reactivity (hereafter the discussion will focus on uranium). On the other hand, uranium complexes in oxidation state (IV) exhibit reactivity attributed mainly to the insertion of reactive molecules (CO, CO₂) into U(IV)-X (X = C, H, heteroatom),⁹ although there are examples of U(III) alkyl complexes with bulky substituents that will also undergo such reactivity rather than promote a redox event.¹⁰ Recently, more attention has been shifted towards higher oxidation complexes (*ie* (V), (VI)) of uranium that historically has been dominated by the chemistry of the uranyl moiety.¹¹ These investigations have led to the isolation of novel compounds with multiple U-E bonds (E = N,¹² O,¹³ S,¹⁴ Se,¹⁴ Te¹⁴) that have not only provided useful insights into the nature of the U-E bond but have also provided novel examples of chemical reactivity.¹⁵ In this context, uranium imido {[U]=NR} complexes have provided an important entry for the study of these higher oxidation¹⁶ states. Landmark examples include: the synthesis and isolation of the U(V) complexes UCp^{Me₃}(=NR) (R=Ph, SiMe₃),¹⁷ the U(VI) complex UCp*₂(=NPh)₂,¹⁸ and more recently the synthesis of imido analogues of the uranyl ion,¹⁹ high valent uranium imido complexes supported by non-innocent ligands,²⁰ as well as the isolation of ‘homoleptic’ U(VI) imido complexes.²¹ These well-defined molecular examples have allowed the study of the nature of the U=NR bond and its relationship to the isoelectronic U=O bond, and have been shown to display a diverse electrochemical behavior. In terms of reactivity towards small molecules, it has been shown that U(V) imido complexes can undergo a metathesis type reaction with CO₂ to release R=N=C=O and produce stable terminal U(V) oxo complexes.²² We have recently described how steric manipulation of the ligand environment around the uranium centre in mixed sandwich complexes can facilitate the isolation of U(V) nitride and terminal oxo complexes,²³ and were thus interested in expanding this chemistry to include the closely related imido derivatives. Herein we report on the synthesis and isolation of U(V) complexes of the type [U]=NR (where [U] is {U[η⁸-C₈H₆(1,4-Si(*i*Pr)₃)₂](Cp*)}), R = SiMe₃, 1-adamantyl, B(2,4,6-Me₃-C₆H₂)₂) and some preliminary investigations into their redox behaviour.

Results and Discussion

Synthesis of [U]=NR complexes

The synthesis of the new [U]=NR complexes ([U] = {U[η⁸-C₈H₆(1,4-Si(*i*Pr)₃)₂](Cp*)}); R = SiMe₃ (**2**), Ad (**3**), BMes₂ (**4**)) can be achieved in a straightforward manner by reaction of the U(III) complex {U[η⁸-C₈H₆(1,4-Si(*i*Pr)₃)₂](Cp*)(THF)} (**1**) with the corresponding azide in hydrocarbon solvents at room temperature (Scheme 1).



Scheme 1: General synthetic route to $[\text{U}]=\text{NR}$ ($[\text{U}] = \{\text{U}[\eta^8\text{-C}_8\text{H}_6(1,4\text{-Si}(\text{iPr})_3)_2](\text{Cp}^*)\}$ complexes.

The new complexes were fully characterised by spectroscopic and analytical methods; their ^1H -NMR spectra feature paramagnetically shifted broad peaks, in agreement with the proposed structures, while in all cases a single broad peak in the region between -60 to -78 ppm was observed in their $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectra. This is shifted downfield in comparison to the U(III) starting material (-133), ^{2a} and is in accordance with the general trend observed upon oxidation of the U(III) metal centre to U(V) but out of the range of +160 to -90 ppm quoted for the seven examples of U(V) complexes compared in this study.²⁴ In the case of **(4)**, the $^{11}\text{B}\{^1\text{H}\}$ -NMR spectrum displayed a very broad signal ($\Delta\nu_{1/2} = 1688$ Hz) centred at 135.86 ppm. Mass spectrometry (EI) showed the expected molecular ions with the correct isotopic distributions and microanalysis was consistent with the molecular formulations, with the exception of **(4)**, where it has been documented that higher deviations from theoretical values are common for boron azides.²⁵ The structures of all three complexes have been confirmed by single crystal X-ray diffraction studies. They are extremely soluble in common hydrocarbons and crystalline solids could only be obtained from SiMe_4 or mixtures of SiMe_4 and n-pentane (see experimental section). Figure 1 shows the ORTEP diagrams of **(2)**, **(3)** and **(4)**, while a comparison of selected bond lengths and angles is given in Table 1.

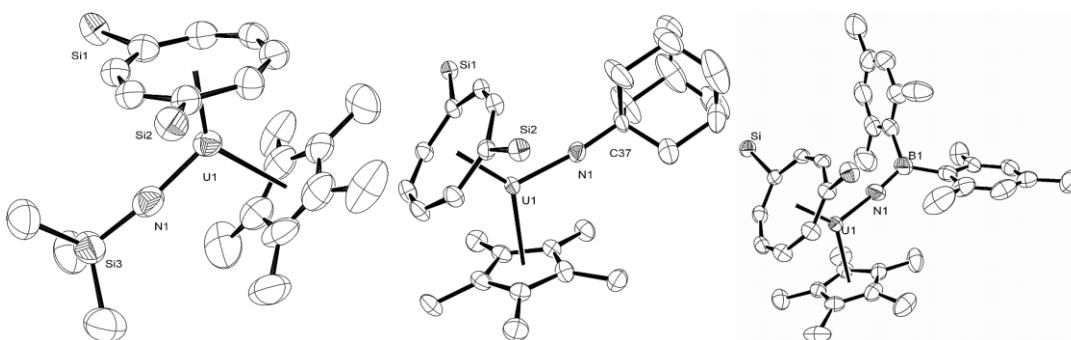


Figure 1: ORTEP diagrams of the molecular structures, from left to right, of **(2)**, **(3)** and **(4)** respectively displaying 50% thermal ellipsoids (hydrogen atoms and iPr groups as well as a molecule of SiMe_4 in the asymmetric unit of **(4)**, have been removed for clarity).

	(2) [U]=NSiMe ₃	(3) [U]=NAd	(4) [U]=NBMe _s ₂
U1-N1 (Å)	1.935(7)	1.964(5)	1.980(4)
R-N1-U1 (°)	172.6(4)	171.7(4)	168.4(4)
Ct(COT)-U (Å)	1.979(7)	1.999(1)	1.983(6)
Ct(Cp*)-U (Å)	2.500(1)	2.515(3)	2.474(9)
Ct(COT)-U-Ct(Cp*) (°)	133.71(3)	133.76(9)	136.16(3)

Table 1: Comparison of key metric parameters of complexes (2), (3) and (4).

The U-N bond distances are characteristic of a U-N multiple bond and are all in the range of 1.90 to 2.12 Å, as previously observed for [U(n)-N(imido)] (n = IV-VI) complexes.^{20, 21, 22, 26} In the case of (2), the U-N bond length is at the shorter end of this range, and also slightly shorter than those found in both (3) and (4). This trend correlates well with the decreasing linearity of the R-N-U moiety in the series ((2) > (3) > (4)) that probably accounts for decreased effective overlap between π orbitals of the uranium centre and the NR ligand, and therefore increasing the U-N bond distances in the series. Furthermore, in the case of (4) elongation of the U-N bond could also be due to π -donation to the empty p orbital located on the boron atom. The R-N-U angles fall well within the range of previously reported values found in [U=NSiMe₃] and [U=NAd] complexes as well as [U=NAr] (160-179° for [U=NSiMe₃], 167-175° for [U=NAd] and 154-180° for [U=NAr]).²⁶ Complex (3) constitutes, to the best of our knowledge, the first example of the NBMe_s₂ (Mes = 2,4,6-Me₃-C₆H₂) imido ligand complexed to an actinide centre and only the second structurally characterised example of this type of imido ligand.²⁷ The N1-B1 distance of 1.417(6) Å is similar within esds to that of 1.404(9) Å in {[(NPN)Ta](μ - η^1 : η^1 -N)[Ta(=N-BC₈H₁₂)(NPN*)]}.²⁸ The Ct(COT)-U-Ct(Cp*) angle in the case of (4) is more obtuse compared to the ones in (2) and (3) (which are the same within esds), probably due to the flexibility of the mesityl substituents to orient themselves in such a way as to minimise steric repulsions.

It is worth noting that the synthesis of both (3) and (4), proceeds with the title compounds being the only observable uranium containing species in solution as evidenced by NMR scale reactions. On the other hand, when a solution of SiMe₃N₃ in C₇D₈ was vacuum transferred to a solution of (1) in the same solvent at -78 °C followed by slow warming to RT, ¹H and ²⁹Si{¹H}-NMR spectroscopy showed the existence of two species in solution in an approximate ratio of 4:1. The major constituent was indeed complex (2) (as evidenced by comparison with an authentic sample) while the minor constituent displayed paramagnetically shifted sharp peaks consistent with a symmetric U(IV) complex. Furthermore, a singlet located at 0.07 ppm was also observed and was

attributed to Si_2Me_6 . Based on these observations, and literature precedents^{26a,g,o} documenting the reductive coupling of the SiMe_3 group upon reaction of $[\text{U(III)}]$ complexes with SiMe_3N_3 and concurrent formation of $[\text{U(IV)-N}_3]$ complexes, we tentatively assigned the afore-mentioned minor species to a U(IV) azide complex (Scheme 2). X-ray diffraction studies confirmed this to be the case and the molecular structure of the bridging azide complex $\{\text{U}[\eta^8\text{-C}_8\text{H}_6(1,4\text{-Si}(\text{iPr})_3)_2](\text{Cp}^*)(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_3)\}_2$ (**5**) is shown in Figure 2, together with selected bond lengths and angles. The latter are unremarkable, falling well within the range of the corresponding values of previously reported $[\text{U}]\text{-N}_3$ complexes,²⁹ and therefore do not warrant further discussion.

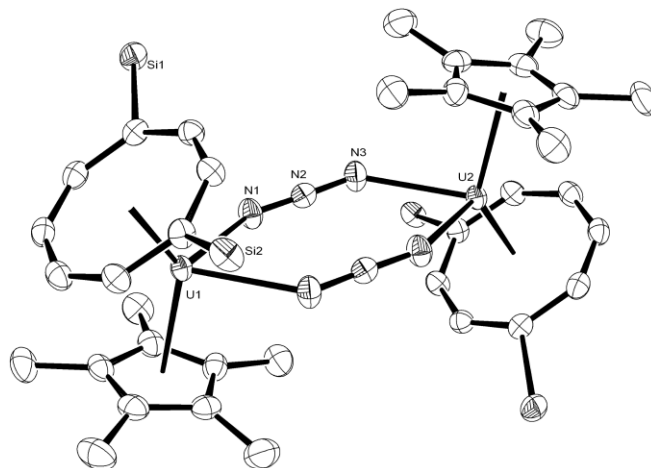
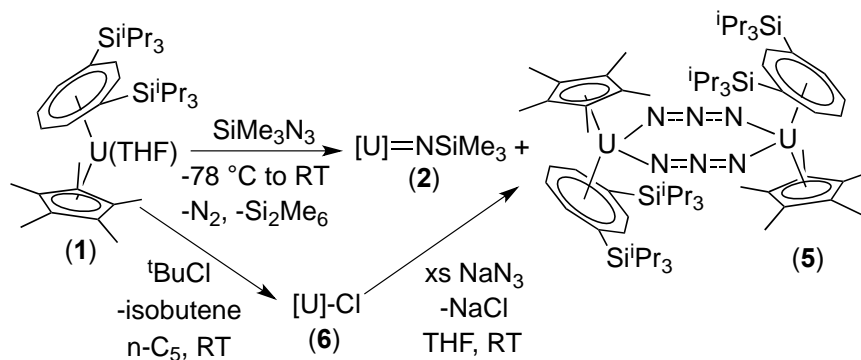


Figure 2: ORTEP diagram of the molecular structure of (**5**) displaying 50% probability ellipsoids (Hydrogen atoms and iPr groups have been omitted for clarity). Selected bond lengths (Å) and angles (°) (the dimer is generated *via* inversion over a centre of symmetry and therefore distances and angles of symmetry equivalent atoms are equal and so omitted): U1-N1 2.490(3), N1-N2 1.165(4), N2-N3 1.176(4), Ct(COT)-U 1.968(8), Ct(Cp*)-U 2.495(1); N2-N1-U1 142.9(3), N1-N2-N3 177.7(4) Ct(COT)-U-Ct(Cp*) 137.36(3).



Scheme 2: Formation of (**5**) as the minor by-product of the synthesis of (**2**) and its independent synthesis from (**6**) and NaN_3 .

Complex **(5)** can be independently synthesised by reaction of $\{U[\eta^8\text{-C}_8\text{H}_6(1,4\text{-Si}(\text{iPr})_3)_2](\text{Cp}^*)\text{Cl}\}$ (**6**)^{9j} with an excess of NaN_3 in THF (Scheme 2). In this case, **(5)** is easily isolated as a dark brown crystalline solid after extraction of the reaction mixture in hot toluene and displays identical spectroscopic (^1H and $^{29}\text{Si}\{^1\text{H}\}$ -NMR) features to that obtained from the reaction of **(1)** with SiMe_3N_3 .

Electrochemical studies

All three imido complexes display a quasi-reversible (over a range of potential scan rates) reduction process at -1.76 V for **(2)**, -1.74 V for **(3)** and -1.62 V for **(4)** vs $\text{Fc}^{0/+}$ (Figure 3), which is attributed to the $\text{U(V)}/\text{U(IV)}$ redox couple in each case.

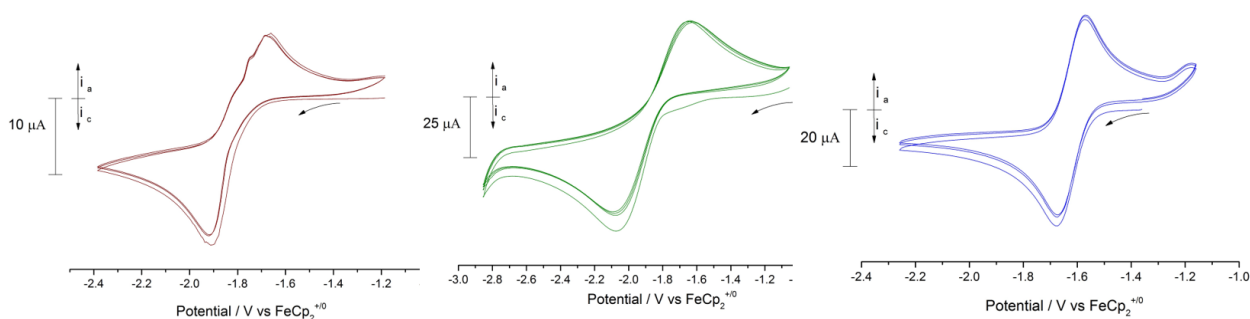


Figure 3: From left to right, overlaid CV scans (3 cycles) in the cathodic direction of **(2)**, **(3)** and **(4)** in 0.05M $[\text{N}(n\text{-Bu})_4][\text{B}(\text{C}_6\text{F}_5)_4]$ in THF (1 mL) (150 mV.s^{-1} scan rate in all three cases). For **(2)** $i_{\text{pa}}/i_{\text{pc}}$ 0.85, $|\Delta E_{\text{pp}}| = 256 \text{ mV}$; for **(3)** $i_{\text{pa}}/i_{\text{pc}}$ 0.94, $|\Delta E_{\text{pp}}| = 425 \text{ mV}$ and for **(4)** $i_{\text{pa}}/i_{\text{pc}}$ 0.96, $|\Delta E_{\text{pp}}| = 293 \text{ mV}$ ($\Delta E_{\text{pp}} = E_{\text{pc}} - E_{\text{pa}}$).

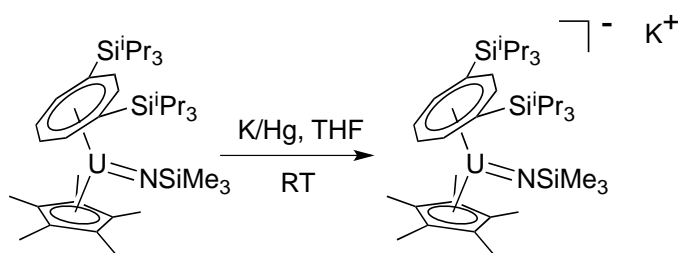
The observed $E_{1/2}$ values for **(2)** and **(3)** are almost identical with that previously reported for the terminal oxo complex $\{U[\eta^8\text{-C}_8\text{H}_6(1,4\text{-Si}(\text{iPr})_3)_2](\text{Cp}^*)=\text{O}\}$ (**7**) (-1.78 V vs $\text{Fc}^{0/+}$),²³ consistent with the isoelectronic relationship between the imido and oxo ligands. These values are more cathodically shifted compared to the corresponding $\text{U(V)}/\text{U(IV)}$ redox potentials for the U(V) imido complexes of the formula $[\text{UN}''_3=\text{NR}]$ ($\text{N}'' = \text{N}(\text{SiMe}_3)_2$, $\text{R} = \text{CPh}_3$, $\text{C}(2\text{-naph})\text{Ph}_2$, $\text{C}(2\text{-naph})_3$, 2-naph) (-1.37 to -1.25 V),^{20c} and rather more cathodically shifted with respect to the observed reduction potentials (-0.34 V to 0.36 V) for the series $\text{UCp}^*_2(=\text{N-Dipp})\text{X}$ (Dipp = 2,6- $\text{iPr}_2\text{-C}_6\text{H}_3$; X = halide, OTf, SPh, CCPh, NPh_2 , OPh, Me, $\text{N}=\text{CPh}_2$).³⁰ Unlike the afore-mentioned compounds, in our case no anodic waves corresponding to an oxidation process were observed over the scanned solvent window.

In the case of **(4)** the measured $E_{1/2}$ value is approximately 0.16 V higher compared to **(2)**, **(3)** and **(7)** meaning that **(4)** is reduced more easily. This is most likely due to the Lewis acidic

boron atom accepting electron density from the nitrogen, thus making the metal centre less electron rich. This observation is also consistent with the explanation for the elongated U-N bond length in the molecular structure of (4).

Chemical reduction of (2)

Based on the voltammograms in Figure 3 (and the precedence of the reduction of (7)²³), the anionic $[U(IV)=NR]^-$ complexes should be chemically accessible. Indeed, in the case of (2) this reduction proceeds very cleanly in the presence of a small excess of K/Hg (0.4-0.5% w/w) within a few minutes in THF as solvent, as evidenced by the colour change from brown to a deep wine-red (see Scheme 3). The 1H -NMR of the reaction mixture (in C_4D_8O) shows the clean conversion to a new species (9) with much sharper resonances. Again, an important diagnostic value was the $^{29}Si\{^1H\}$ NMR which displayed a signal centred at -159.6 ppm attributed to the Si^iPr_3 groups (the $NSiMe_3$ signal could not be located). The $^{29}Si\{^1H\}$ -NMR shift follows the trend (*ie* shifted upfield compared to (2) (-70.6 ppm)) observed for the reduction of $\{U[\eta^8-C_8H_6(1,4-Si(iPr)_3)_2](Cp^*)O\}$ (7) with K/Hg to yield $\{U[\eta^8-C_8H_6(1,4-Si(iPr)_3)_2](Cp^*)(\mu-O)K(18-c-6)\}$ (18-c-6 = 18-crown-6) (8), and is in fair agreement with the corresponding $^{29}Si\{^1H\}$ -NMR spectrum of the latter (-172.2 ppm).²³



Scheme 3: Synthesis of (9)

Red crystals of (9) suitable for a single crystal X-ray diffraction study were obtained from slow evaporation of a 2:1 C_6H_6/Et_2O solution at room temperature, and the molecular structure is shown in Figure 4 (left), together with selected bond lengths and angles.

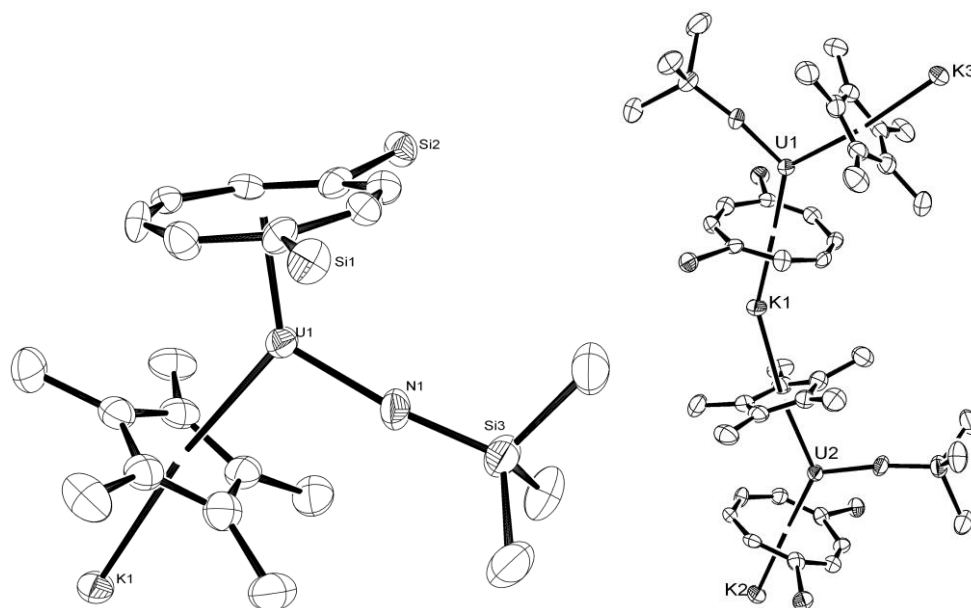


Figure 4: ORTEP diagram of the molecular structure of **(9)** (left) and its extended structure in the solid state (right) (50% probability ellipsoids). Hydrogen atoms, half a molecule of C₆H₆ and ⁱPr groups have been removed for clarity. Selected bond lengths (Å) and angles (°): U1-N1 1.972(5), N1-Si3 1.712(5), U1-Ct(Cp*) 2.599(4), U1-Ct(COT) 2.066(4), K1-Ct(Cp*) 2.788(4), K1-Ct(COT) 2.466(5) ; Ct(COT)-U1-Ct(Cp*) 172.1(5), U1-N1-Si3 172.7(4), Ct(Cp*)-K1-Ct(COT) 156.5(1), U2-Ct(Cp*)-K1 176.5(8), K1-Ct(COT)-U1 176.4(7).

The U-N bond (1.972(5) Å) in the anionic complex **(9)** is slightly elongated compared to that in the parent complex **(2)** (1.935(7) Å); a similar phenomenon has been observed with the lengthening of the U-O bond upon the reduction of **(7)** (see above). Nevertheless, this bond is still in the range of U-N multiple bonds observed for [U(n)=N(imido)] (n = IV-VI) complexes. Similarly the U-Ct(Cp*) and U-Ct(COT) in **(9)** are elongated compared to **(2)**, while the Ct(Cp*)-U-Ct(COT) angle in **(9)** (172.1(5)°) is significantly more obtuse compared to that in **(2)** (133.71(3)°). On the other hand, the U-N-Si angle remains unchanged, signifying the role of the imido moiety as a spectator ligand. These pronounced differences in the metric parameters of the mixed sandwich unit could be due to the need to accommodate the K⁺ counter-ion in the coordination sphere of the anion, in the absence of a coordinating terminal heteroatom as is the case for **(8)**.²³ Indeed, this results in the formation of an extended polymeric structure in the solid state (Figure 4, right), in which the K⁺ cations are bridging the mixed uranium sandwich units through the aromatic ring systems. The U-Ct(Cp*/COT)-K angles are almost linear while the Ct(COT)-K-Ct(Cp*) angle is 156.5(1)°. Remarkably, when the reaction is repeated in the presence of 18-crown-6 in THF, **(9)** is still the only compound isolated after work-up. Furthermore, the ¹H-NMR signals attributed to **(9)** generated *in-situ* remain unchanged both in the presence or the absence of 18-crown-6 in C₄D₈O, further

confirming that the crown-ether is not able to disrupt the K^+ cation environment in solution. Nevertheless, since (**9**) is only soluble in (the presence of) THF, the formation of species where the intercalation of the potassium ion between the two carbocycles is disrupted by coordinating THF, cannot be excluded; nevertheless, the isolation of crystals of (**9**) in the presence of Et_2O suggests that if such an interaction exists in solution then it is very weak. Unfortunately (**9**) could not be isolated as a microanalytically pure compound as it is thermally unstable; pink-red crystalline material has the tendency to convert into an as yet unidentifiable brown non-crystalline solid, with concomitant ligand decomposition.

When (**3**) was reduced in the same manner (**2**), a colour change to brown red was observed; in the case of (**4**) when the reduction was carried out in a non-coordinating solvent (*e.g.* toluene) the almost instant formation of a red precipitate was observed. Unfortunately, in both cases we have not managed to isolate well-defined complexes but initial spectroscopic evidence (sharper signals in the 1H -NMR spectra consistent with reduction to U(IV)) suggests that similar reactivity to that of (**2**) is occurring.

Conclusions

In summary, we have reported the synthesis of three new U(V) mixed sandwich imido complexes via the straightforward reaction of the [U(III)] precursor $\{U[\eta^8-C_8H_6(1,4-Si(^iPr)_3)_2](Cp^*)(THF)\}$ (**1**) with organic azides. In one case ($SiMe_3N_3$), reductive coupling of the azide occurs as a parallel minor reaction pathway to form Si_2Me_6 and the U(IV) bridging azide complex $\{[U](\mu-N_3)\}_2$ along with the expected U(V) $[U]=NSiMe_3$ complex. All three imido complexes show a quasi-reversible reduction between -1.6 to -1.75 V, and in one case clean chemical reduction has been achieved using K/Hg to readily afford $K^+\{U[\eta^8-C_8H_6(1,4-Si(^iPr)_3)_2](Cp^*)=NSiMe_3\}^-$. The latter displays a novel, extended structure in the solid state in which K^+ counter cations are sandwiched between the Cp^* ligand and the COT^{tips2} ligand of neighbouring anionic mixed sandwich uranium units, a structural feature that persists even when the synthesis is carried out in the presence of 18-crown-6.

Acknowledgements

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Experimental:

General Procedures:

All manipulations were carried out in a MBraun glovebox under N₂ or Ar (O₂ and H₂O <1 ppm) or by using standard Schlenk techniques under Ar (BOC pureshield) passed through a column containing BASF R3-11(G) catalyst and activated molecular sieves (4 Å). All glassware was dried at 160 °C overnight prior to use. Filter cannulas were prepared using Whatman 25 mm glass microfiber filters and were predried at 160 °C overnight. THF and toluene were dried over molten K and distilled under a N₂ atmosphere and were kept in Young ampoules over activated molecular sieves (4 Å) or a potassium mirror, respectively, under Ar. Hydrocarbons were dried over NaK, distilled under a N₂ atmosphere, and kept in Young ampoules over a potassium mirror under Ar. SiMe₄ (≥99%) was purchased from Aldrich, degassed by three freeze–thaw cycles and dried by stirring over NaK for three days before being vacuum distilled and kept over molecular sieves (4 Å) in an Ar glovebox at -35 °C. Deuterated toluene, benzene, and THF were degassed by three freeze–thaw cycles, dried by refluxing over K for 3 days, vacuum distilled, and kept in Young ampoules in the glovebox under N₂. {U[η⁸-C₈H₆(1,4-Si(ⁱPr)₃)₂](Cp*) (THF)}^{2a} and {U[η⁸-C₈H₆(1,4-Si(ⁱPr)₃)₂](Cp*)Cl}⁹ were prepared according to literature. SiMe₃N₃ was purchased from Aldrich, was degassed by three freeze–thaw cycles and kept in a Young's ampule at 5 °C under Ar. AdN₃ was purchased from Aldrich and was kept in an Ar glovebox in a -35 °C freezer and used as received. (2,4,6-Me₃-C₆H₂)₂BN₃ was prepared by modification of a published literature procedure (see below). ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR data were recorded on a Varian VNMR S400 spectrometer operating at 400 MHz (¹H). The spectra were referenced internally to the residual protic solvent (¹H) or the signals of the solvent (¹³C). ²⁹Si{¹H} NMR spectra were referenced externally relative to SiMe₄. All spectra were recorded at 30 °C unless otherwise stated. EI-MS mass spectra were recorded on a VG-Autospec Fisons instrument at the University of Sussex unless otherwise stated. Elemental analyses were performed at the Microanalysis Service of the School of Chemistry at University of Bristol. Cyclic voltammetry studies were performed in an Ar filled glovebox using a BaSi-Epsilon potentiostat under computer control. CV experiments were performed using the three electrode method with glassy carbon (7 mm²) as the working electrode, Pt wire as the counter electrode and Ag wire as the pseudo-reference one. Sample solutions were prepared by dissolving the electrolyte ([N(n-Bu)₄][B(C₆F₅)₄]) in 1 mL of THF (0.05M) followed by the analyte to give a concentration of the latter of *ca* 5 mM. The reported half potentials are referenced to the Fc^{0/+} redox couple, which was measured by adding ferrocene (*ca* 1 mg) to the sample solution.

(2,4,6-Me₃-C₆H₂)₂BN₃: 300 mg (2,4,6-Me₃-C₆H₂)₂BF (1.12 mmol) (purchased from TCI and stored under Ar in a -35 °C freezer) were placed in a Young's ampoule containing a glass-coated magnetic follower in an Ar glovebox. To this, 2 mL of SiMe₃N₃ (d = 0.868 mg/μL; 15.06 mmol) were added to produce a heterogeneous reaction mixture that after overnight stirring became homogeneous. The reaction was followed by ¹H-NMR by dissolving small aliquots in C₆D₆ (the ¹¹B{¹H}-NMR signals of the product and the starting material are broad and are both centred at *ca* 54 ppm). Full conversion to the title compound was observed after 7 days of stirring at RT, upon which time volatiles were removed in vacuum to give (2,4,6-Me₃-C₆H₂)₂BN₃ as a white flocculent crystalline solid which was kept in a glovebox under N₂. Yield: 300 mg (92%). ¹H-NMR (δ C₆D₆, 400MHz): 2.09 (s, 6H, *p*-CH₃), 2.27 (s, 12H, *o*-CH₃), 6.71 (s, 2H, aromatic). EI-MS: 291 [M], 263 [M-N₂], 248 [M-N₃], 172 [M-C₉H₁₁], 144 [MesBN], 119 [C₉H₁₁], 116 [BMes-Me]
 NOTE: ¹H-NMR for Mes₂BF in C₆D₆ is as follows: ¹H-NMR (δ C₆D₆, 400MHz): 2.10 (s, 6H, *p*-CH₃), 2.28 (s, 6H, *o*-CH₃), 2.29 (s, 6H, *o*-CH₃), 6.70 (s, 2H, aromatic).

Scaling up this preparation was not undertaken as boron azides are potentially highly energetic materials.

{U[η⁸-C₈H₆(1,4-Si(^{*i*}Pr)₃)₂](Cp*)}₂=NSiMe₃} (**2**): 500 mg (0.58 mmol) of {U[η⁸-C₈H₆(1,4-Si(^{*i*}Pr)₃)₂](Cp*)(THF)} were dissolved in *ca* 10 mL of n-pentane in an Ar glovebox with vigorous stirring and were treated with 80 μL (1.04 mol eq) of TMSN₃ in 2 portions at RT. During addition effervescence was observed and a colour change from black brown to dark brown-orange. After 10 minutes of stirring volatiles were removed and the residue was extracted in SiMe₄ (*ca* 10 mL) and filtered through a glass-microfibre filter pipette in an Ar glovebox. The SiMe₄ extract was let to evaporate slowly at RT to *ca* 2 mL before being placed at -35 °C overnight to produce the title compound as a dark brown crystalline solid in two crops. Yield: 360 mg (*ca* 71%). ¹H-NMR (δ C₇D₈): -5.97 (s, 18H, CH(CH₃)₂), -4.84 (s, 6H, CH(CH₃)₂), -4.30 (s, 18H, CH(CH₃)₂), -1.80 (s, 15H, C₅(CH₃)₅), 20.36 (s, 9H, Si(CH₃)₃), the COT CH protons could not be observed; ²⁹Si{¹H}-NMR (δ C₇D₈): -70.61 (s, broad) the NSiMe₃ signal could not be observed; EI-MS: 877 (M), 741 (M-Cp*), 460 (M-COT^{tips2}), 444 (M-COT^{tips2}-Me), 115 (H(Si^{*i*}Pr₃)₂); Elem. Anal.: Calcd for C₃₉H₇₂NSi₃U: C 53.39; H 8.27; N 1.60. Found: C 53.67; H 8.32; N 1.78.

In situ reaction of {U[η⁸-C₈H₆(1,4-Si(^{*i*}Pr)₃)₂](Cp*)(THF)} with SiMe₃N₃: A solution of 25 mg (0.029 mmol) {U[η⁸-C₈H₆(1,4-Si(^{*i*}Pr)₃)₂](Cp*)(THF)} in C₇D₈ (0.4 mL) in a Youngs NMR tube was degassed and cooled at -78 °C and to that was vac-transferred a degassed solution of 4 μL (1.04 mol eq) TMSN₃ in *ca* 0.2 mL C₇D₈. Upon warming to RT effervescence was observed and the ¹H-NMR

spectra were recorded to show formation of (2) and (5) in approximately 80:20 ratio respectively.

$\{U[\eta^8-C_8H_6(1,4-Si(iPr)_3)_2](Cp^*)_2=NAd)\}_2$ (3): This was done as for (2) starting from 550 mg (0.638 mmol) of $\{U[\eta^8-C_8H_6(1,4-Si(iPr)_3)_2](Cp^*)(THF)\}$ and 113 mg (1 mol eq) AdN_3 added in small portions over *ca* 5 minutes. After effervescence had ceased, the dark brown solution was stripped of volatiles and the residue was dissolved in $SiMe_4$ (*ca* 5 mL) and filtered through a glass-microfibre filter pipette. Insoluble in $SiMe_4$ solids were taken in a *ca* 1:1 mixture of $nC_5/SiMe_4$ and filtered as above (total volume 5 mL). Both solutions upon slow evaporation started depositing crystals after *ca* 20 minutes and the crystallisation was completed by overnight refrigeration at $-35\text{ }^\circ\text{C}$. Yield: 390 mg (65%). 1H -NMR (δ C_7D_8): -5.91 and -5.44 (broad d, 42H, $CH(CH_3)_2$), 1.24 (broad s, 15H, $C_5(CH_3)_5$), 10.91 (s, 3H, adamantyl), 13.67 (s, 3H, adamantyl), 17.74 (s, 3H, adamantyl), 29.16 (broad s, 6H, adamantyl) the COT CH protons could not be observed; $^{29}Si\{^1H\}$ -NMR (δ C_7D_8): -76.08 (s, Si^iPr_3); EI-MS: 938 (M), 803 (M- Cp^*), 522 (M-COT^{tips2}), 388 (UNAd), 157 ($(Si^iPr_3)_3$), 135 (Cp^*), 115 ($H(Si^iPr_3)_2$); Elem. Anal.: Calcd for $C_{46}H_{78}NSi_2U$: C 58.82; H 8.37; N 1.49. Found: C 58.99; H 8.44; N 1.87

$\{U[\eta^8-C_8H_6(1,4-Si(iPr)_3)_2](Cp^*)_2=NBMe_2)\}_2$ (4): A Young's ampoule was charged with 100 mg (0.116mmol) of $\{U[\eta^8-C_8H_6(1,4-Si(iPr)_3)_2](Cp^*)(THF)\}$ and 33.7 mg (1 mol eq) of Mes_2BN_3 in an Ar glovebox and C_6H_6 (*ca* 5 mL) was added to produce a dark brown red solution. After effervescence had ceased, volatiles were removed in vacuum and the residue extracted in $SiMe_4$ (*ca* 4 mL) and let to slowly evaporate to approximately half before being refrigerated at $-35\text{ }^\circ\text{C}$ overnight to yield the title compound the $SiMe_4$ solvate. Yield: 50 mg (*ca* 38%). 1H -NMR (δ C_7D_8): -4.18 (s, 18H, $CH(CH_3)_2$), -2.44 (broad s, 24H, $CH(CH_3)_2$), 2.78 (broad s, 15H, $C_5(CH_3)_5$), 4.50 (s, 6H, Mes- CH_3), 8.56 (broad s, 6H, Mes- CH_3), 11.20 (s, 6H, Mes- CH_3) the COT CH proton could not be observed; $^{29}Si\{^1H\}$ -NMR (δ C_7D_8): -63.05; $^{11}B\{^1H\}$ -NMR (δ C_7D_8): 135.86 (broad s, $\Delta\nu_{1/2} = 1688\text{ Hz}$); EI-MS: 1053 (M), 1011 (M- iPr), 637 (M-COT^{tips2}), 517 ((M-COT^{tips2}-Mes), 416 (COT^{tips2}), 373 (UC p^*), 265 (UNBMes₂), 157 ($(Si^iPr_3)_3$), 115 ($H(Si^iPr_3)_2$); Elem. Anal.: Calcd for $C_{54}H_{85}BNSi_2U.SiMe_4$: C 61.03; H 8.57; N 1.23. Found: C 58.87; H 8.38; N 2.14 repeated attempts from re-crystallised batches of different syntheses gave irreproducible nitrogen analyses.

NOTE: The low yield is probably due to the high solubility of the product in apolar solvents. When the reaction was repeated on a NMR scale the product was found to be present in solution in >85% yield.

Independent synthesis of $\{U[\eta^8-C_8H_6(1,4-Si(iPr)_3)_2](Cp^*)(\mu-N_3)\}_2$ (5): A young's ampule was charged with 100 mg (0.121 mmol) of $\{U[\eta^8-C_8H_6(1,4-Si(iPr)_3)_2](Cp^*)Cl\}$ (6) and 15 mg (1.9 mol

eq) NaN₃ and THF (*ca* 10 mL) was added to it to give a dark red solution. The reaction mixture was stirred overnight at RT to adopt a dark brown colouration. Volatiles were removed in vacuum and the residue was extracted with hot toluene (3x5 mL) and filtered while warm *via* a filter cannula. Upon cooling brown crystals started forming which were isolated by filtration, washed with nC₅ (5 mL) and dried in vacuum. Reducing the supernatant and washing and cooling at -80 °C produced a second crop. Yield: 75 mg (74.5%). ¹H-NMR (δ C₇D₈): -82.43 (s, 4H, CH), -76.69 (s, 4H, CH), -6.09 (s, 36H, CH(CH₃)₂), -3.79 (s, 12H, CH(CH₃)₂), -0.95 (s, 36H, CH(CH₃)₂), 8.10 (s, 30H, C₅(CH₃)₅), 60.78 (s, 4H, CH); ²⁹Si{¹H}-NMR (δ C₇D₈): -74.57 (s, Si^{*i*}Pr₃). Elem. Anal.: Calcd for C₇₂H₁₂₆N₆Si₄U₂: C 51.96; H 7.63 N 5.05. Found: C 52.12; H 7.84; N 5.14

K⁺{U[η⁸-C₈H₆(1,4-Si(*i*Pr)₃)₂][Cp*](=NSiMe₃)₂}⁻ (9): 100 mg (0.114 mmol) of (2) were dissolved in 0.5-0.7 mL of C₄D₈O in an Ar glovebox and with stirring K/Hg amalgam (0.4% w/w) (2-3 drops *ca* 5 fold excess) was added. After a few minutes the brown solution adopted a deep red colouration and the solution was carefully decanted from the amalgam using an elongated Pasteur pipette. After NMR were collected, the solvent was quickly removed in vacuum and the residue taken in a 2:1 mixture of C₆H₆/Et₂O (*ca* 3 mL) in an Ar glovebox, and the solvent removed in vacuum slowly until red crystals suitable for single crystal XRD started forming. ¹H-NMR (δ-C₄D₈O): -19.28 (s, 6H, CH(CH₃)₂), -16.78 (s, 18H, CH(CH₃)₂), -11.73 (s, 18H, CH(CH₃)₂), -9.89 (s, 15H, C(CH₃)₅), 41.78 (br s, 9H, Si(CH₃)₃), the COT CH protons could not be observed; ²⁹Si{¹H}-NMR (δ-C₄D₈O): -159.6 (s, Si(*i*Pr)₃) the NSiMe₃ signal could not be observed; No molecular ion could be observed in ESI⁻ mode. No elemental analyses could be obtained from the sample as the red crystalline material readily decomposes to a yet unidentified brown compound.

X-ray Crystallography

The datasets for (5) was collected on a Bruker-Nonius KappaCCD area detector diffractometer with a sealed-tube source (Mo *Kα*) and an Oxford Cryosystems low-temperature device (173 K), operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect,³¹ Scalepack, and Denzo.³² Absorption corrections were based on equivalent reflections using SADABS.³³ In the case of (4) data were collected using an Agilent Gemini Ultra diffractometer with an Enhance source (Mo *Kα*) equipped with an Eos CCD area detector and the same temperature device as above. The strategy used for data collection is the same as previously. Control, integration and absorption correction were handled by the CrysAlis Pro software. In the case of (2) and (3), data were collected using the same Agilent single crystal diffractometer as above with an Enhance Ultra source (Cu *Kα*). Control, integration and absorption correction were handled by the CrysAlis Pro software. In the case of (9) data were collected on a

Rigaku MicroMax-007 HF rotating anode (Cu $K\alpha$) equipped with VariMax HF confocal mirrors at 100 K. Control of the instrument was handled by the d-Trek software and the data set was processed after its collection using the CrysAlis Pro software suite. In the case of **(3)** a numerical absorption correction based on gaussian integration over a multifaceted crystal model was applied. The crystals were mounted on a glass fiber with silicon grease or MiTiGen loops, from dried vacuum oil kept over 4 Å in a MBraun glovebox under Ar. All solutions and refinements were performed using the WinGX³⁴ package and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model. CCDC deposition numbers 1570061-1570065 for **(2)**- **(9)**, respectively . Crystal structure and refinement details are given in the following table:

Compound	(2)	(3)	(4)	(5)	(9)
Colour, Habit	Brown, Block	Black, Plate	Brown, Plate	Brown, Block	Red, Block
Size/mm	0.4x0.4x0.1	0.3x0.2x0.05	0.2x0.1x0.05	0.10x0.08x0.04	0.01x0.04x0.08
Empirical Formula	C ₃₉ H ₇₂ N ₁ Si ₃ U	C ₄₆ H ₇₈ NSi ₂ U ₁	C ₅₄ H ₈₅ BNSi ₂ U . C ₄ H ₁₂ Si	C ₃₆ H ₆₃ BN ₃ Si ₂ U	C ₃₉ H ₇₂ KNSi ₃ U. 0.5 C ₆ H ₆
M	877.28	939.30	1141.47	832.10	955.43
Crystal System	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	15.0573(5)	10.2067(4)	11.9433(5)	12.094(2)	11.7331(2)
<i>b</i> /Å	12.6837(4)	21.2821(6)	13.3855(6)	13.714(3)	17.4554(3)
<i>c</i> /Å	22.2295(6)	20.7383(8)	21.2151(10)	13.886(3)	22.8082(4)
α /°	90	90	73.292(4)	69.64(3)	90
β /°	96.978(3)	99.814(4)	76.515(4)	66.55(3)	98.008(2)
γ /°	90	90	65.798(4)	66.92(3)	90
<i>V</i> / Å ³	4214.0(2)	4438.9(3)	2937.0(3)	1892.8(7)	4625.70(14)
<i>Z</i>	4	4	2	2	4
μ /mm ⁻¹	12.079	11.021	2.859	4.378	11.614
T (K)	173(2)	173(2)	173(2)	173(2)	100(2)
θ min/max	2.96/70.196	2.998, 70.079	3.417, 26.372	3.42, 27.35	3.2, 67.080
Completeness	99.0 to 70.196	98.2 to 70.079	99.1 to 26.372	98.2 to 27.35	97.3 to 67.080
Reflections Total/Independent	7432/6872	8274 / 7255	11911/ 10458	8418/7445	7136/8024
<i>R</i> _{int}	0.0428	0.0765	0.0375	0.0445	0.0489
Final <i>R</i> 1 and <i>wR</i> 2	0.0501 and 0.1339	0.0431 and 0.1096	0.0419 and 0.1008	0.0305 and 0.0658	0.0448 and 0.1258
Largest peak hole/ e.Å ⁻³	1.901 and - 2.179	3.335 and - 2.323	2.502 and - 0.968	1.386 and - 0.856	1.595 and - 2.345
ρ _{calc} /g.cm ⁻³	1.383	1.406	1.291	1.460	1.372

Table 2. Crystal structure and refinement details

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